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01/09/2002 - 08:23:29
(1) CA 274911

(12) Patent:

(54) METHANOL CATALYST

(54) CATALYSEUR DE METHANOL

Information on this page:

(72) Inventors (Country): GROVER BLOOMFIELD (Not Available)
JOHN C. WOODRUFF (Not Available)

(73) Owners (Country): THE COMMERCIAL SOLVENTS CORPORATION

(71) Applicants (Country):

(74) Agents:

(45) Issued on: Oct. 25, 1927

(22) Filed on:

(43) Laid open on:

(52) Canadian Class (CPC): 252/83

(51) International Class (IPC): N/A

Parent Country/Inventor Treaty (PCT): No

(30) Application priority date: None

Availability of abstract: N/A
Language of filing: Unknown

ABSTRACT:

CLAIMS: Show a listing

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

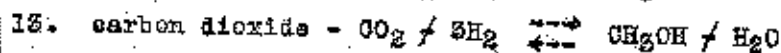
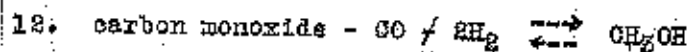
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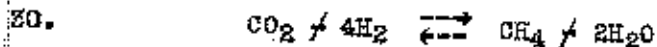
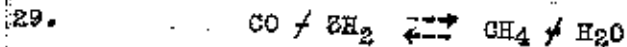
1. Our invention relates to the production of
 2. methanol by the high pressure catalytic combination of
 3. oxides of carbon with hydrogen, and pertains more
 4. directly to the preparation and employment of improved
 5. catalysts in the process.

6. Methanol may be produced by combining oxides
 7. of carbon with hydrogen in the presence of a suitable
 8. catalyst at elevated temperature and pressure. Carbon
 9. monoxide, carbon dioxide, and mixtures of the two oxides
 10. may be employed, these substances reacting with hydrogen
 11. according to the following reactions:-



14. It is observed that when carbon dioxide is the
 15. oxide employed, one molecule of water is formed for
 16. every molecule of methanol produced. On the other
 17. hand when pure carbon monoxide is used, theoretically
 18. there is nothing produced by the reaction but methanol.
 19. Actually in practice pure carbon monoxide and pure
 20. carbon dioxide are both difficult to obtain economically,
 21. so that the methanol synthesis is carried out by react-
 22. ing a mixture of carbon monoxide and carbon dioxide
 23. with hydrogen.

24. In addition to the reactions producing methanol
 25. there are, in the methanol synthesis, undesirable side-
 26. reactions which cut down the yield of the desired
 27. product. The principal side reaction which may occur
 28. is the formation of methane, which is illustrated below:



31. In addition to the methane side-reaction
 32. there are other side-reactions which sometimes occur

1. in which there are produced esters, aldehydes, organic
2. acids, ketones, and hydrocarbons other than methane;
3. these reactions occurring as the result of the poly-
4. merization or condensation of methanol or its decompo-
5. sition products.

6. When a gas mixture comprising carbon oxides
7. mixed with an excess of hydrogen over the amount
8. theoretically required to produce methanol is passed
9. over a catalytic substance consisting of metallic oxides
10. at a pressure above 100 atmospheres and at a temperature
11. above 250° C. there is nearly always produced some
12. reaction between the gaseous components. The extent of
13. this reaction depends to some degree on space velocity,
14. temperature, and pressure, but the fact remains that
15. under the conditions outlined, carbon oxides and hydrogen
16. react to some extent in all cases.

17. The substances formed by such a process depend,
18. both as to identity and as to amount, almost entirely
19. on the nature and activity of the catalytic substance
20. present. The methanol catalysts mentioned in prior
21. patents and literature are combinations of metals or
22. their oxides which substances normally exert a hydrogen-
23. ating catalytic effect on gas reactions.

24. Without exception the literature on the high
25. pressure catalytic process for synthesizing methanol
26. definitely states that the presence of iron or any of
27. its compounds in a catalyst destroys or poisons the
28. catalyst and inhibits methanol formation. While iron is
29. an excellent hydrogenating catalyst for many reactions,
30. in some forms it reacts with carbon monoxide, and with
31. mixtures of hydrogen and the carbon oxides (i.e. carbon
32. monoxide and/or carbon dioxide) used in the methanol

1. reaction, forming a volatile carbonyl compound and
2. inhibiting the methanol reaction. The normal effect of
3. the presence of iron in a methanol catalyst is to cause
4. the reaction of hydrogen and carbon oxides to produce
5. only methane.

6. We have now discovered a method of employing
7. iron in a methanol catalyst whereby the desirable
8. hydrogenating catalytic effect of the iron is obtained
9. and the tendency to methane formation is inhibited.
10. In preparing our improved catalyst we employ a mixture
11. of magnesium oxide and ferric hydroxide. Magnesium oxide
12. - per se - has no catalytic effect on the methanol re-
13. action, while ferric hydroxide - per se - has a positive
14. inhibiting effect. Nevertheless, when these two
15. ingredients are properly compounded a desirable methanol
16. catalyst is produced.

17. We have discovered that when ferric hydroxide
18. obtained by precipitation of iron from a ferric salt in
19. aqueous solution is incorporated with magnesium oxide and
20. the mass is dried and broken up into granules the result-
21. ant material produces an active catalyst for the
22. synthetic methanol reaction. While we are certain that
23. in the presence of the hydrogen and carbon oxide gas
24. mixtures used for synthesizing methanol the ferric hydro-
25. xide is subsequently reduced to iron oxide and possibly
26. in part to iron - per se - the exact structure of the
27. resultant catalyst is not known to us.

28. The amount of ferric hydroxide may vary from
29. 3% to 25% of the weight of magnesium oxide, though we
30. prefer to use about 10%. The magnesium oxide may be
31. incorporated with ferric hydroxide in any convenient
32. manner as is indicated in the appended examples.

Example I

1. 313 grams of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
2. is dissolved in 25 liters of water which is then heated
3. to 95°C . To the hot solution is added 750 grams of
4. magnesium oxide with stirring 190 cubic centimeters of
5. 12.38 Normal Ammonium hydroxide is added to precipitate
6. the iron to the hydroxide form. The mixture is allowed
7. to stand, the supernatant liquid siphoned off, and the
8. mass is filtered and washed until there is no test for
9. nitrates in the filtrate.

10. The mass is then completely dried and broken
11. up into granules, whereupon it is ready for use.

12. It will be observed that the final composition
13. of this catalyst after precipitating the iron and drying
14. the mass is approximately 750 grams magnesium oxide and
15. 82 grams of ferric hydroxide.

Example II

16. 350 grams of ferric nitrate is dissolved in
17. 5 liters of water and sufficient ammonium hydroxide is
18. added to precipitate all of the iron as ferric hydroxide.
19. The resultant flocculent mass is thoroughly washed with
20. water and after decanting the excess water, 900 grams of
21. magnesium oxide is thoroughly mixed therewith. The
22. mixture is then dried and broken up into granules.

Example III

23. In place of the ferric nitrate mentioned in
24. Example I and II an equivalent quantity of another
25. soluble ferric salt may be employed.

26. When a mixture of 90% hydrogen gas with 10%
27. oxides of carbon, comprising about 7% carbon dioxide and
28. 3% carbon monoxide is passed over 1000 cubic centimeters
29. of catalyst granules thus prepared at a pressure of
30. 2000 pounds at a temperature of about $350-450^\circ \text{C}$., and

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1. at a space velocity of about 75,000 there will be
2. produced, hourly, about 1.5 liters of condensate contain-
3. ing about 65% of methanol, the remainder of the conden-
4. sate being substantially pure water. Increase of
5. pressure and increase of space velocity over the figures
6. given in the example increase the total amount of con-
7. densate per hour whereas an increase in the percentage
8. of carbon monoxide produces an increase in the percent-
9. age of methanol in the condensate.

10. If pure carbon monoxide is employed as the
11. carbon oxide the percentage may be advantageously
12. increased to 20%, the hydrogen being correspondingly
13. diminished.

14. Now having described our invention we claim
15. the following as new and novel:
16. 1. A methanol catalyst comprising magnesium
17. oxide and ferric hydroxide.
18. 2. A methanol catalyst comprising 97 - 75%
19. magnesium oxide and 3 - 25% ferric hydroxide.
20. 3. A methanol catalyst comprising magnesium
21. oxide and ferric hydroxide, the ferric hydroxide being
22. formed by precipitation in aqueous solution from a
23. soluble ferric salt.
24. 4. A methanol catalyst comprising 97 - 75%
25. magnesium oxide and 3 - 25% ferric hydroxide, the ferric
26. hydroxide being formed by precipitation in aqueous
27. solution from a soluble ferric salt.
28. 5. A methanol catalyst comprising 750 grams
29. of magnesium oxide and 82 grams of ferric hydroxide, the
30. ferric hydroxide being formed by precipitation in
31. aqueous solution from a soluble ferric salt.
32. 6. A process for the preparation of a
33. methanol catalyst which comprises precipitating ferric
34. hydroxide from an aqueous solution of a ferric salt on
35. magnesium oxide.

1. 7. A process for the preparation of a methanol
2. catalyst which comprises precipitating from 3 - 25% of
3. ferric hydroxide from an aqueous solution of a ferric
4. salt on 97 - 75% of magnesium oxide.
5. 8. A process for the preparation of a
6. methanol catalyst which comprises mixing magnesium oxide
7. with an aqueous solution of a ferric salt, precipitating
8. ferric hydroxide by adding ammonium hydroxide, filter-
9. ing, washing, and drying the resultant mass.
10. 9. A process for the preparation of a
11. methanol catalyst which comprises dissolving 313 grams
12. of ferric nitrate in 25 liters of water, adding 750
13. grams of magnesium oxide, precipitating the iron as
14. ferric hydroxide by adding ammonium hydroxide, and re-
15. covering the resultant mass in dry form.
16. 10. A process for the production of synthetic
17. methanol which comprises passing a mixture of hydrogen
18. and carbon oxides at a pressure in excess of 50
19. atmospheres and at a temperature of 350 - 450° C. over
20. a catalyst initially containing magnesium oxide and
21. ferric hydroxide, cooling the reacted gases, and recover-
22. ing the resultant methanol.
23. 11. A process for the production of synthetic
24. methanol which comprises passing a mixture of hydrogen
25. and carbon oxides at a pressure in excess of 50
26. atmospheres and at a temperature of 350 - 450° C. over
27. a catalyst initially containing 97 - 75% magnesium oxide
28. and 3 - 25% ferric hydroxide, cooling the resultant
29. gases, and recovering the resultant methanol.